Two-dimensional charge carrier recombination in amorphous poly- and oligo-thiophenes

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1 Outline

1. Bimolecular recombination in amorphous organic semiconductors.
2. Spatially correlated landscape of random energy.
3. Mean disorder approximation.
4. Recombination in 2D systems: lamellas.
5. Basic recombination features.
6. Conclusion.

2 Motivation

► Basic processes in electronic organic devices are charge carrier injection, transport, and recombination. (apart from the case of pure monopolar transport)
► In comparison to the injection and charge transport, recombination is much less studied both theoretically and experimentally.
► 2D recombination is very different from the usual 3D recombination. We suggest a simple model for the consideration of 2D recombination in amorphous organic semiconductors having spatially correlated energy landscape.

3 Langevin recombination
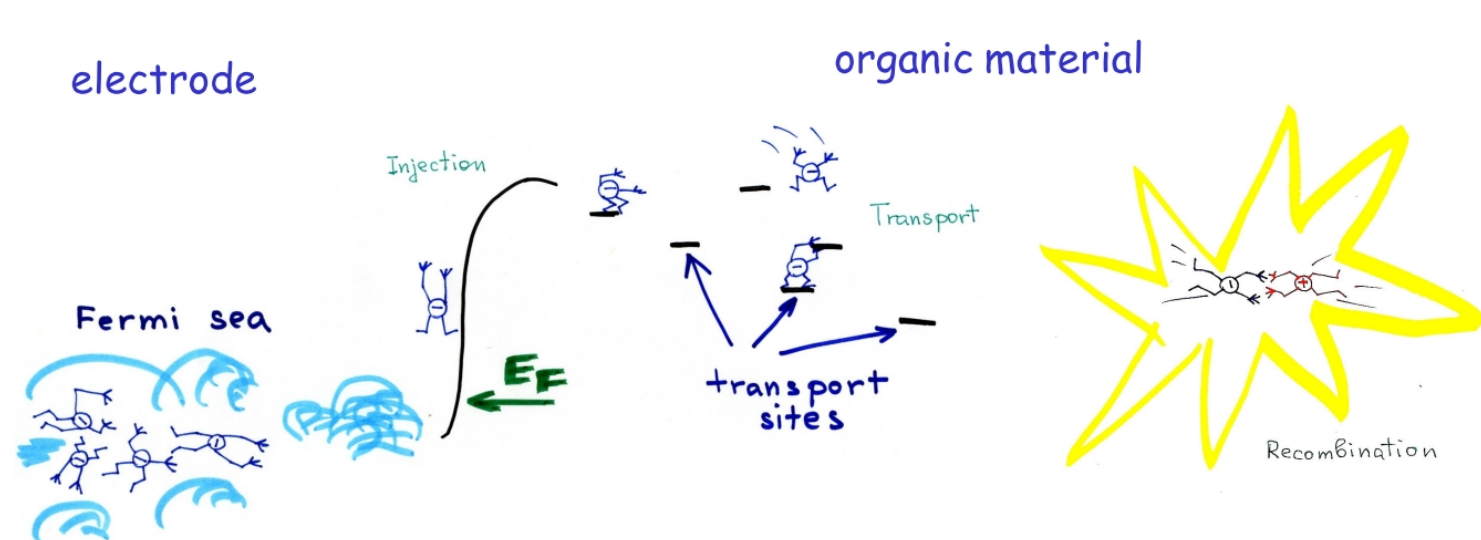
Bimolecular recombination kinetics $e^+ + e^- \rightarrow \emptyset$

$$\frac{d(n,p)}{dt} = -\gamma np$$

For diffusion-limited recombination in the uniform medium without disorder Paul Langevin obtained the relation

$$\gamma = \gamma_L = \frac{4\pi e}{\varepsilon}\left(\mu_+ + \mu_-\right)$$

P. Langevin, Ann. Chim. Phys. **28**, 433 (1903), the paper is still actively cited.

4 Long range correlations in amorphous organic materials

Specific feature of the random energy landscape in amorphous organic semiconductors is a strong spatial correlation of the energies of transport sites, while the density of states typically has the Gaussian form. For example, in polar materials with the dominant contribution of the dipolar electrostatic disorder the correlation function $C(\mathbf{r}) = \langle U(\mathbf{r})U(0)\rangle /\sigma^2 \simeq A\frac{a}{r}$, $\sigma^2 = \langle U^2\rangle$, a is the intermolecular distance, $A \simeq 1$ depends on the details of the arrangement of molecules at short distances.
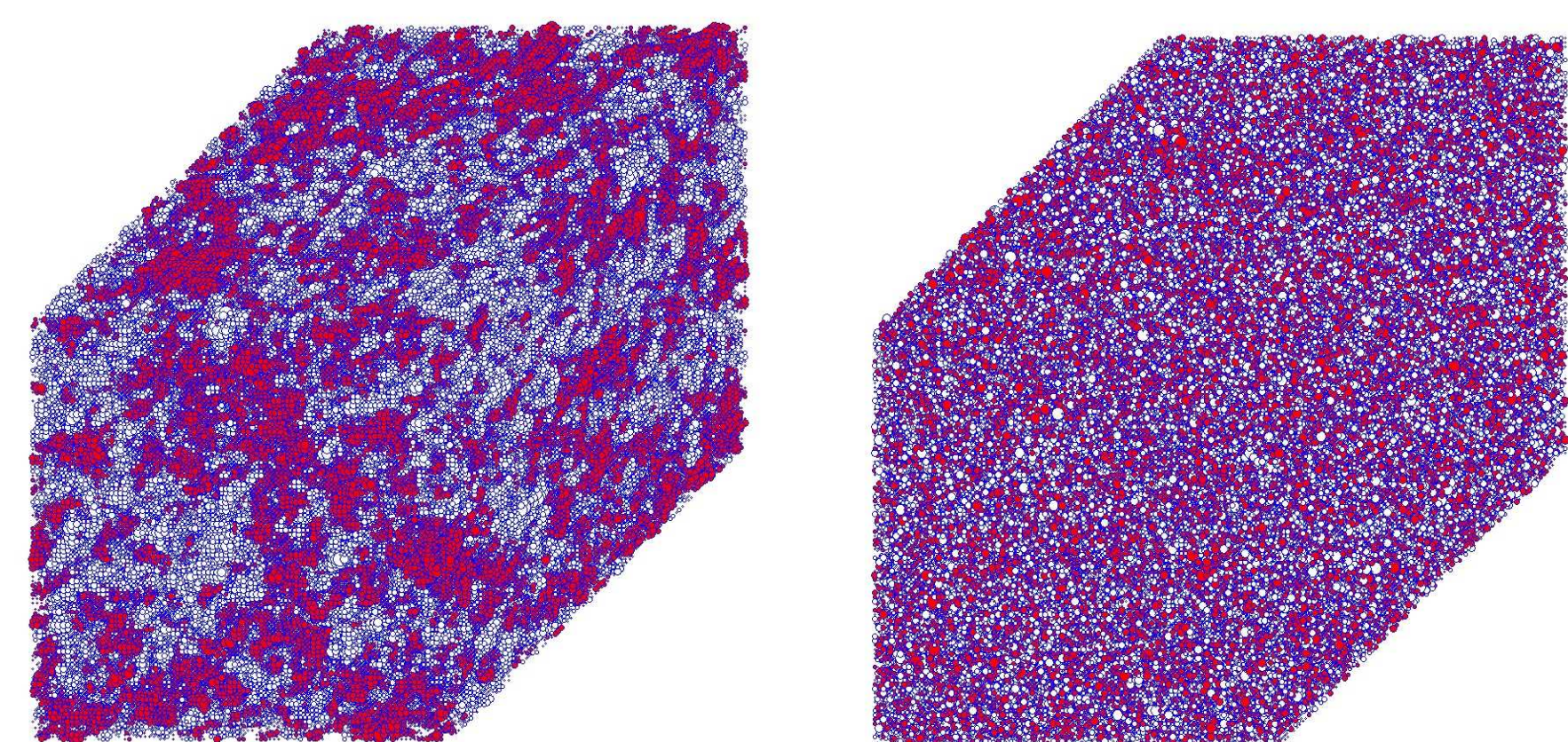

Dipole glass   Non-correlated disorder

Circles of different colors indicate sites with carrier energies of different signs, and the size of the circle is proportional to the absolute value of the energy.

Correlated disorder in amorphous semiconductors also may be provided by the contribution of the conformational disorder; for example from the fluctuation of the angles in spiropiranes (A. Massè et al, Phys. Rev. B, **95**, 115204 (2017))).

5 Effective interaction between charge carriers in amorphous materials (example of the dipole glass)
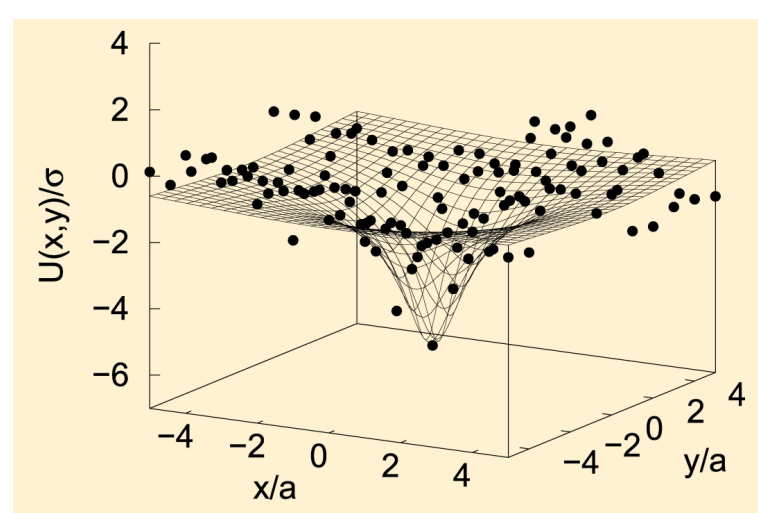
Two-dimensional cross section near a deep trap, dots are random carrier energies at the nodes.
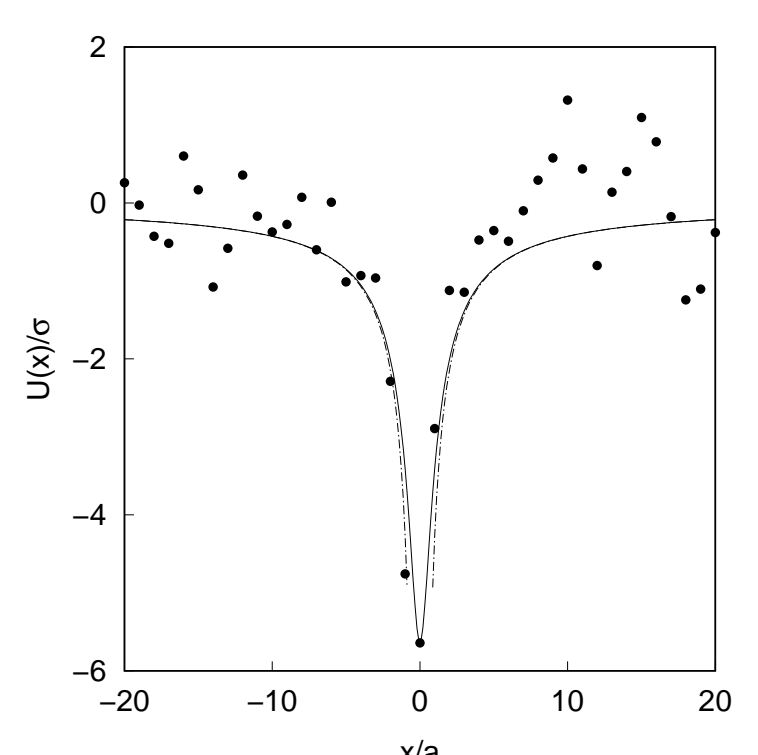
One-dimensional cross-section near a deep trap; solid line is a graph of $-UC(r)/\sigma^2$, dotted line is a graph of $-0.76Ua/r$, where $|U|$ is the depth of the trap.

The decisive approximation: we replace the random potential for the electron with an averaged one taking into account the hole sitting in a well with the bottom at U. Then we take the average over U. The figure shows the profile of the averaged well.

Energy of interaction of an electron with a complex "captured hole + potential well organized by a random medium" for the dipole glass model (as a particular example)

$$U(\mathbf{r}) = -\frac{e^2}{\varepsilon r} + UC(\mathbf{r}) \simeq -\frac{e^2}{\varepsilon r} - U\frac{Aa}{r}$$

6 Why we suggest a 2D recombination?

Ordinary kinetics of the bimolecular recombination (assuming the equal concentration of electrons and holes)

$$\frac{dn}{dt} = -\gamma n^2 \;\Rightarrow\; n(t) = \frac{n_0}{1 + \gamma n_0 t} \;\Rightarrow\; n(t) \propto t^{-1},\; t \to \infty$$

In poly- and oligo-thyophenes another kinetcs is frequently observed

$$n(t) \propto t^{-b},\; b < 1$$

and formally we may describe it by

$$\frac{dn}{dt} = -\widetilde{\gamma}n^{2+s},\; b = \frac{1}{1+s}$$

At the same time in such materials planar lamellar structures do exist with the thickness ≈ 1.5 nm having huge anisotropy ot the mobility $\frac{\mu_{\text{in plane}}}{\mu_{\text{out of plane}}} \simeq 100$ (H. Sirringhaus et al., Nature, 1999, 401, 685–688).

We assume that the recombination takes place in 2D lamellas, then the exponent $s > 0$ naturally occurs for the diffusion-limited kinetics.

7 How to treat 2D recombination?

Traditional calculation of the rate constant of diffusion-controlled reactions means calculating it in a stationary state (assuming there is an inexhaustible source of material at infinity, which makes it possible to establish such a state). In this situation we can take the limit $n \to 0$ and calculate the true reaction rate constant.

In the stationary state the outflow of the material due to reaction is $\Delta_- \propto \gamma t$, and the maximal possible inflow is $\Delta_+ \propto (Dt)^{d/2}$, while for the development of the stationary state we need $\Delta_-/\Delta_+ \to 0$, hence it requires $d > 2$.

For $d \leq 2$ "the rate constant" goes to 0 for $n \to 0$ and may in the complex way (not by the power law) depend on n. The situation becomes even more complicated if we take into account the effect of disorder.

To remove the nullification of γ we introduce the cut-off at $R_l = R(n_R/n)^{1/2}$, where R is the recombination radius, n is the carrier density and $n_R \simeq 1/R^2$ is the limit density.

8 2D Recombination rate constant for relaxed carriers in a Gaussian density of states

$$\gamma = \frac{n_R}{(2\pi\sigma^2)^{1/2}\,n}\int_{-\infty}^{\infty} dU\,\gamma[U_{\text{eff}}]\frac{\exp\left(-\frac{U^2}{2\sigma^2}\right)}{1+\exp\left(\frac{U-\mu}{kT}\right)}$$

$$U_{\text{eff}}(r) = -\frac{e^2}{\varepsilon r} \pm UC(r)$$

Sign "+" here is for the attractive (conformational) disorder, and sign "-" is for the repulsive (electrostatic) disorder.
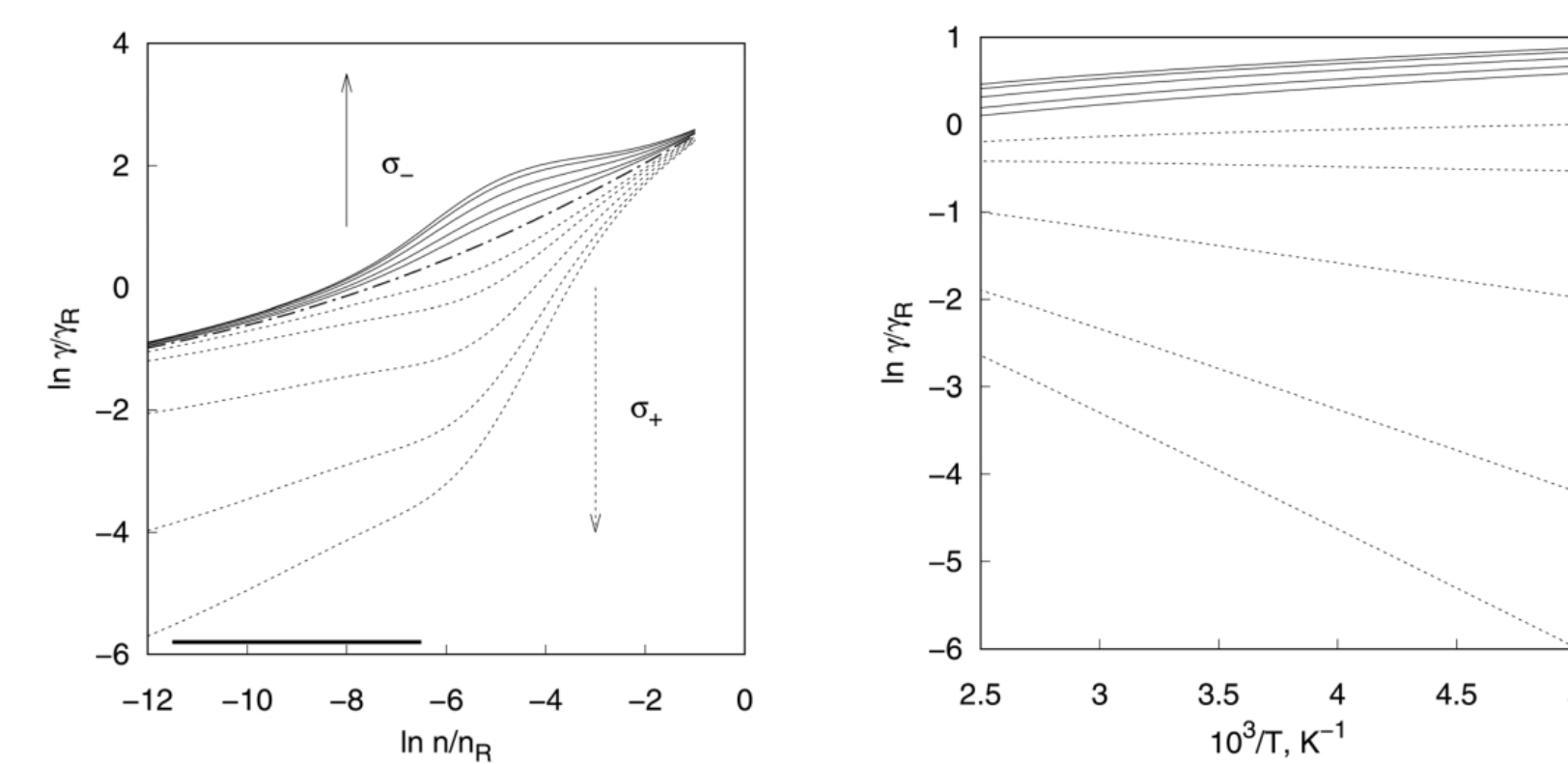
$$\gamma[U] = 2\pi D \frac{\exp\left[\beta U(R_l)\right]}{\int_R^{R_l}\frac{dr}{r}\exp\left[\beta U(r)\right]}$$

$D = D_+ + D_-$ is the sum of the diffusivities,

R is the recombination radius,

$\beta = 1/kT,\quad R_l = R(n_R/n)^{1/2}$,

9 Typical dependences of γ on carrier density and temperature

Here $\varepsilon = 3$ and σ varies from 0.05 eV to 0.15 eV for different curves, $R = 1$ nm and for the density plot $T = 300$K; $\gamma_R = 2\pi D$, σ_+ means the repulsive disorder, and σ_- the attractive one. Dot-dashed line shows the corresponding dependence for the no disorder case. Thick bar at the abscissa axis indicates the typical range of n in experiments.

10 The most significant conclusions

► For a low dimensional diffusion-limited kinetics a simple procedure has been suggested for the approximate calculation of the bimolecular recombination rate constant.
► This procedure provides a natural generalization for the calculation of the rate constant for the recombination of charge carriers in the random medium (e.g., amorphous organic semiconductors).
► Spatial correlation of the random energy landscape is a reason for the complicated dependence of the rate constant on the carrier density.
► Dependence of the rate constant on the carrier density and temperature has been studied.

11 Papers

S.V. Novikov, Bimolecular Recombination of Charge Carriers in Polar Amorphous Organic Semiconductors: Effect of Spatial Correlation of the Random Energy Landscape. J. Phys. Chem. C **122**, 22856 (2018)

S.V. Novikov, Enhanced Bimolecular Recombination of Charge Carriers in Polar Amorphous Organic Semiconductors: Overcoming the Langevin Limit. J. Phys. Chem. C **123**, 18854 (2019)

S.V. Novikov, Two-dimensional bimolecular recombination in amorphous organic semiconductors. Phys. Chem. Chem. Phys. **21**, 1174 (2020)